Phenol degradation by Fenton's process using catalytic in situ generated hydrogen peroxide

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ABSTRACT

The recent reported pathway using oxygen and formic acid at ambient conditions has been utilized to generate hydrogen peroxide in situ for the degradation of phenol. An alumina supported palladium catalyst prepared via impregnation was used for this purpose. Almost full destruction of phenol was carried out within 6 h corresponding to the termination of 100 mM formic acid at the same time. In addition, a significant mineralization (60%) was attained. A simulated conventional Fenton process (CFP) using continuous addition of 300 ppm H_2O_2 displayed maximum 48% mineralization. Study of different doses of formic acid showed that decreasing the initial concentration of formic acid caused faster destruction of phenol and its toxic intermediates. The catalytic in situ generation of hydrogen peroxide system demonstrated interesting ability to oxidize phenol without the addition of Fenton's catalyst (ferrous ion). Lower Pd content catalysts (Pd1/Al and Pd0.5/Al) despite of producing higher hydrogen peroxide amount for bulk purposes, did not reach the same efficiency as the Pd5/Al catalyst in phenol degradation. The later catalyst showed a remarkable repeatability so that more than 90% phenol degradation along with 57% mineralization was attained by the used catalyst after twice recovery. Higher temperature (45 °C) gave rise to faster degradation of phenol resulting to almost the same mineralization degree as obtained at ambient temperature. Meanwhile, Pd leaching studied by atomic adsorption proved excellent stability of the catalysts.

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1. Introduction

Chemical oxidation and its developed form, advanced oxidation processes (AOPs) have been assigned an outstanding priority over other wastewater treatment methods e.g. adsorption and stripping techniques, due to their ability to mineralize organic pollutants. Different possible routes for OH$^\bullet$ radicals production such as Fenton and Fenton-like offered by AOPs cover wide range of treatment processes with specific conditions [1,2]. Among the various approaches of generation of hydroxyl radical, Fenton reaction is one of the cleanest and most efficient processes to eliminate particularly toxic compounds in wastewaters and soil as well [3]. Fenton reaction involves generation of hydroxyl radical via hydrogen peroxide and ferrous ion, known as Fenton's reagent [2]. The application of Fenton's reagent as an oxidant for wastewater remediation is attractive due to the fact that iron is a highly abundant and non-toxic element, and hydrogen peroxide breaks down to environmentally benign products [4].

In the last decades, there has been great interest to produce hydrogen peroxide in situ within the reaction medium in order to promote efficiency of the subsequent oxidation reaction and lowering the relevant costs of hydrogen peroxide transportation as well [5–16]. In situ produced hydrogen peroxide can be consumed prior to decomposition to H_2O and O_2 leading to higher yield and selectivity toward the favorite reaction direction. In addition, the oxidation process would be proceeded under an appreciable controlled rate due to the lack of undesired bulk feeding of hydrogen peroxide. The in situ generating approaches should be specifically designed according to the physical and the chemical features of the subsequent oxidation process. Initially, the systems containing hydrogen and oxygen as substrates and metal-supported-titanium-silicate (TS-1) as catalyst were offered for hydroxylation and epoxidation purposes [5,7,8]. Afterwards, the conversion of benzene to phenol over palladium membrane presented by Niwa et al. displayed a break-through in in situ generation of H_2O_2 demonstrating an outstanding selectivity (up to 97%) for phenol [11]. Recently, oxidation of propane has been carried out with high selectivity toward oxygenates compounds through gold supported TS-1 [15,16]. In all above cases, the reaction mechanism is strongly postulated to be passing through an H_2O_2 intermediate. Indeed, the assumption has been evidenced by the direct generation of hydrogen peroxide from H_2 and O_2 over the similar catalytic systems [17,18]. However, the common point of the above studies is to use H_2–O_2 mixture which involves an

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inherent risk of explosion. To eliminate this drawback, replacing H_2 with a safer source could be an interesting alternative. Hydrazine and hydroxylamine have been offered for such a purpose but neither can be considered as a suitable replacement for hydrogen due to their toxicity or explosivity [19,20]. Very recently, we have reported a simple, clean and environment-friendly route for the generation of hydrogen peroxide via formic acid and oxygen [21]. In this method, formic acid (as replacement for H_2) and oxygen at full ambient conditions react over a supported-Pd catalyst leading to hydrogen peroxide generation. One of the main advantages of this new approach is its ability to be applied for in situ purposes. As referred above, there are several works related to chemically in situ generation of hydrogen peroxide, but concerning degradation of organic pollutant compounds, other than few reports [22], the rest of the works have been mostly carried out through electrochemical processes [23].

In this work, we demonstrate the application of in situ hydrogen peroxide generated from formic acid and oxygen for degradation of phenol as model pollutant compound. In fact, in this process, hydrogen peroxide is consumed as soon as it is produced to oxidize phenol. The efficiency of the system is measured as phenol decomposition rate during the reaction and the amount of total organic carbon (TOC) removed as well. The effect of factors such as temperature and catalyst Pd content is studied. A comparison between our system and continuous and batch CFP is carried out.

2. Experimental

2.1. Catalyst preparation and characterization techniques

The alumina supported-Pd catalysts with Pd content range 0.1–5 wt% (denoted as Pd0.1/Al, Pd0.5/Al, Pd1/Al, Pd2.5/Al and Pd5/Al, respectively) were synthesized through conventional impregnation. An acidic solution of $PdCl_2$ was added to a slurry solution of γ-Al_2O_3 (prepared by sol–gel). The mixture was stirred and aged for 1 h. Water was removed by rotary vapor at 55 °C. The precipitate was dried at 110 °C and then was calcined at 400 °C for 3 h. Finally, the catalyst was reduced under a flow of pure hydrogen (20 ml min^{-1}) at 200 °C for 2 h.

The catalysts were characterized by X-ray powder diffraction (XRD), N_2 adsorption and H_2 chemisorption. X-ray diffraction of the samples was carried out using a Siemens D5000 diffractometer by nickel-filtered Cu Kα radiation. The patterns were recorded over a range of 2θ angles from 5° to 70°. In all the patterns, as summarized in Table 1, the broad peaks corresponding to the structure of γ-Al_2O_3 can be observed. The characteristic reflections of Pd(0) are recognizable clearly only in the pattern of Pd5/Al sample. N_2 adsorption was performed using a Micromeritics ASAP 2010 apparatus at 77 K. First, the samples were degasified at 120 °C for 12 h. Total surface area was calculated by the BET method. As shown in Table 1, pure γ-Al_2O_3 has a surface area nearly 400 m^2 g^{-1}. Impregnation with the $PdCl_2$ acidic solution and the subsequent treatments cause a slump in the surface area of the final synthesized samples. H_2 chemisorption was also acquired by

a Micromeritics ASAP 2010. Before analysis at 100 °C, a pretreatment program including evacuation at 100 °C, oxidation under O_2 flow at 350 °C, evacuation at 100 and 350 °C, reduction under H_2 flow at 350 °C and evacuation at 100 °C respectively was fulfilled. Metal dispersion was obtained by the ratio of the gas (H_2) uptake to the total Pd content assuming an adsorption stoichiometry of H:Pd = 1:1. Particle size of the catalysts was calculated by the following equation [24]:

$$d_{VA} = \frac{6(\upsilon_m/a_m)}{D}$$

where d_{VA} is the mean particle size, υ_m is the volume occupied by an atom m (for Pd is 14.70 Å^3), a_m is the surface area occupied by an atom m on a polycrystalline surface (for Pd is 7.93 Å^2) and D is the metal dispersion.

2.2. Catalytic tests

The phenol degradation reactions were implemented at ambient conditions (25 °C and atmospheric pressure) in a magnetically stirred three-necked glass reactor with a capacity of 100 ml. The reaction details are as follows unless it is mentioned specifically. The volume of the reaction was always 50 ml containing phenol (100 ppm), ferrous iron (10 ppm) and the catalyst (0.1 g). Formic acid was injected with different concentrations (40–500 mM). The initial pH of the solution was 2.2–2.5 depending on the formic acid concentration. Oxygen was passed bubbling into the reaction medium with a flow rate of 20 ml min^{-1}. The temperature of the reaction was controlled using a water bath. Without any exception, all the reactions were performed at darkness in order to avoid any interfering effect of existing light. Phenol degradation and formic acid decomposition were monitored by sampling at regular time intervals and analysing by high performance liquid chromatography HPLC (Shimadzu LC-2010 equipped with a SPD-M10A Diode array UV-vis detector). A Varian OmniSpher C18 column and a solution containing Milli-Q H_2O and acetonitrile (60:40) at pH 3.80 adjusted by phosphoric acid as mobile phase were used to analyse phenol and the aromatic intermediates at wavelength 254 nm. An Acclaim OA column and a mobile phase containing 100 mM Na_2SO_4 at pH 2.65 adjusted by methanesulphonic acid were used to analyse organic acid at wavelength 210 nm. TOC for each sample was measured by a Shimadzu TOC-5000A. The reaction solution at the end of each run after filtration was analysed by atomic absorption spectroscopy to detect leached Pd.

Continuous Fenton's reaction for phenol degradation was simulated using almost the same reaction conditions (100 ppm phenol, 10 ppm Fe^{2+}, adjusted pH 3–3.5 and ambient conditions) as we used for the in situ ones. For this purpose, 300 or 600 ppm H_2O_2 was injected continuously via a peristaltic pump (Watson-Marlow 205CA) during a period of 6 h. In the batch experiments, a total of 300 or 600 ppm H_2O_2 was injected concurrently into the solution (with the above mentioned conditions) at the start of the reaction and the reaction proceeded for 1 h. For each run, sampling was carried out at regular time intervals.

3. Results and discussion

3.1. Hydrogen peroxide generation from formic acid and O_2

Hydrogen peroxide can be produced through the reaction of formic acid and oxygen over supported-Pd catalysts [21]. The process is carried out within completely ambient conditions and attains a respectable productivity. Simply, formic acid is catalytically decomposed into CO_2 and H_2 and simultaneously O_2 reacts with released H_2 to form H_2O_2. Although another assumption of

Table 1
Textural and structural properties of the synthesized catalysts.

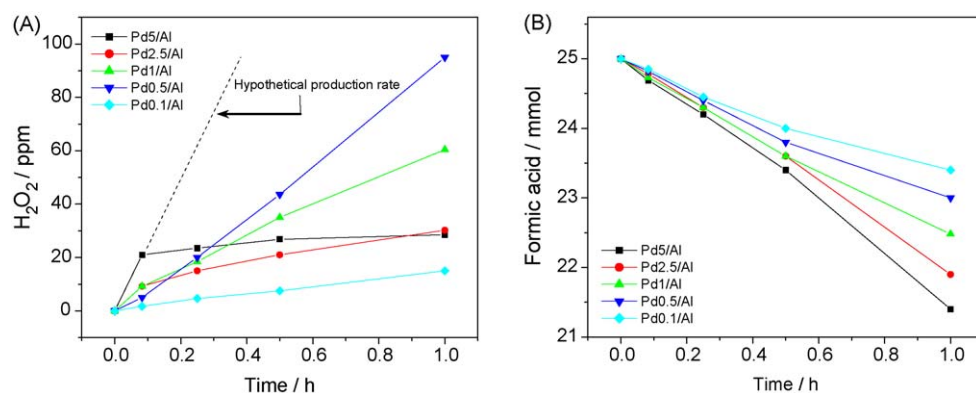| Catalyst	Pd loading (wt%)	XRD phases	BET (m^2 g^{-1})	D (%)	d_{VA} (nm)
γ-Al_2O_3	0	γ-Al_2O_3	389	–	–
Pd0.1/Al	0.1	γ-Al_2O_3	218	26.7	4.2
Pd0.5/Al	0.5	γ-Al_2O_3	224	25.2	4.4
Pd1/Al	1.0	γ-Al_2O_3	214	19.9	5.6
Pd2.5/Al	2.5	γ-Al_2O_3	206	12.8	8.7
Pd5/Al	5	Pd(0), γ-Al_2O_3	205	5.8	19.2

Fig. 1. (A) H_2O_2 formation profile during the reaction of O_2 and formic acid over Pd/Al catalysts at ambient conditions. (B) Formic acid decomposition profile over Pd/Al catalysts during H_2O_2 formation reaction.

direct reaction of O_2 with formic acid resulting to H_2O_2 should be taken into account. The results of generation of hydrogen peroxide from formic acid and oxygen shown in Fig. 1A demonstrate a sharp rate of hydrogen peroxide formation for the highest Pd content catalyst (Pd5/Al) at 5 min of the reaction. The rate becomes moderate through the reaction time till 1 h, demonstrating severe competition between formation and decomposition of hydrogen peroxide. This high production value at 5 min can reflect somewhat real activity of the catalyst for the generation of hydrogen peroxide, because by proceeding the reaction it seems that the decomposition of H_2O_2 overcomes its generation. Therefore we can hypothesize a theoretical production rate of H_2O_2 by extrapolating the line passing through the points at 0 and 5 min. Decreasing the Pd content to 0.1% leads to reducing of H_2O_2 production at 5 min whereas an outstanding promotion is observed after 1 h reaction markedly for the Pd0.5/Al catalyst (as high as 100 ppm H_2O_2). Over lower Pd content catalysts, the H_2O_2 formation profile becomes closer to linearity during the whole reaction. In general, over the catalyst, two favorable reactions occur, i.e. decomposition of formic acid and formation of hydrogen peroxide, depending the progress of the later on the rate of the former. Nevertheless, the side reactions of H_2O formation, H_2O_2 decomposition to H_2O and O_2 and H_2O_2 hydrogenation to H_2O influence the productivity and the selectivity of the reaction undesirably. Referring to the metal particle size of the catalysts presented in Table 1, it can be seen that the catalysts with smaller Pd particles are able to generate hydrogen peroxide in 1 h with higher rate than the ones with bigger particles, despite of the higher Pd content loaded on the later ones. On the other hand, increasing Pd content results to higher decomposition rate of formic acid (Fig. 1B). Taking into consideration of such a complicated system, the optimum Pd0.5/Al catalyst is offered for the bulk production of hydrogen peroxide within 1 h reaction. But as our main purpose is to generate H_2O_2 in situ for the subsequent oxidation reaction, that catalyst may not be the adequate one, because for the in situ application, higher production rate at short time is of high importance. Hence, the Pd5/Al catalyst can be more eligible for the above purpose than the other ones due to its ability to decompose formic acid with higher rate and further production of hydrogen peroxide at short times.

3.2. Phenol degradation

Assuming the Pd5/Al as the most appropriate catalyst for the in situ application, the phenol degradation reactions were performed at full ambient conditions and using that and ferrous ion as Fenton's catalyst. The concentration of ferrous ion was elected according to the limits established by Directive 91/271/CE, which

is 10 mg l^{-1}. Since degradation of toxic compounds at low concentrations (especially less than 100 ppm) is of high importance [25], we conducted all our reactions starting with a solution containing 100 ppm phenol.

The main results have been summarized in Table 2. Different initial doses of formic acid were fed into the reaction medium. During direct generation of hydrogen peroxide an initial concentration of 500 mM was found to be favorable. Decreasing that amount to lower ones caused reducing the yield of the process. Contrarily, in situ generated hydrogen peroxide initiated with 500 mM formic acid leads to maximum 88% degradation of phenol after 6 h, and no complete consumption of formic acid is attained, whereas decreasing initial concentration of formic acid to 100 mM results in almost full degradation of phenol and no formic acid remains within the reaction medium. It seems that during in situ generation of hydrogen peroxide high concentration of formic acid may deactivate the catalyst to degrade phenol by avoiding phenol to be exposed to the generated hydrogen peroxide or by consumption of generated H_2O_2 or $OH^\bullet$ by formic acid itself. Entire disappearance of formic acid from the solution enabled us to analyse TOC utterly associated to phenol degradation process and thereupon to monitor the phenol mineralization achieved by the system. Based on that, a 60% mineralization was gained after 6 h. Further reducing the initial concentration of formic acid down to 60 and 40 mM, leads to the entire decomposition of formic acid after 5 and 4 h and the mineralization degrees are 58 and 55%, respectively. By termination of formic acid, oxidation of phenol obviously diminishes, while mineralization proceeds up to 66% after 6 h. The reason can be the extended decomposition of the intermediates, in particular carboxylic acids, over the catalyst.

Considering 14 mol H_2O_2 required for the entire mineralization of phenol (according to the reaction below):
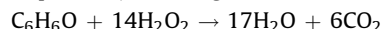
$$C_6H_6O + 14H_2O_2 \rightarrow 17H_2O + 6CO_2$$

Table 2
Phenol degradation results obtained using in situ generated H_2O_2 over the Pd5/Al catalyst.

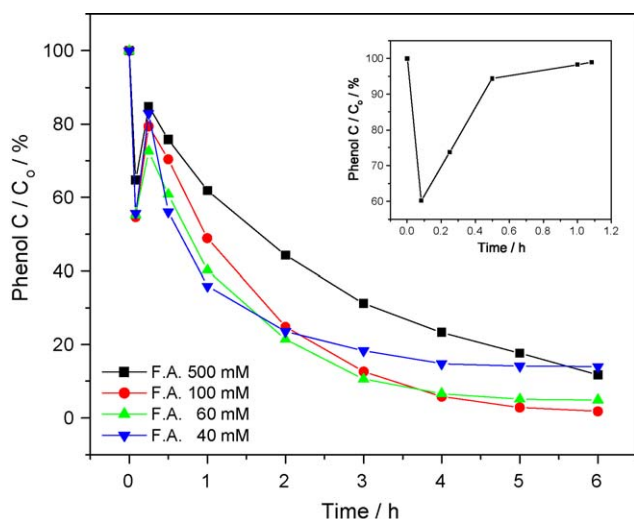| Run no.	F.A. int. conc. (mM^a)	t (h)	F.A. conv. (%)	Phenol conv. (%)	TOC removed (%)
1	500	6	33	88.3	N.A.
2	200	6	69	94.8	N.A.
3	100	6	100	98.2	60.7
4	60	5	100	94.9	57.9
		6	100	95.1	66.3
5	40	4	100	82.5	55.3
		6	100	86.3	66

^{a} Formic acid initial concentration.

Fig. 2. Phenol degradation profile using in situ generated H_2O_2 at different initial concentrations of formic acid. Inset: variations of phenol concentration in presence of only 0.1 g Pd5/Al catalyst.

and 60% mineralization achieved, an approximate amount of 300 ppm H_2O_2 is estimated that has been produced through the in situ process. The number represents the apparent amount of produced H_2O_2 which has thoroughly participated in the mineralization of phenol. The real amount of the generated H_2O_2, which definitely must be much more than 300 ppm, is indistinct. A great part of H_2O_2 is decomposed as soon as generated, may be consumed to oxidize the formic acid feed, or to oxidize phenol and intermediates without any mineralization. Fig. 2 displays the phenol degradation profiles using different initial doses of formic acid during a reaction time of 6 h. At 5 min, a sharp decreasing–increasing of phenol concentration is observed which can be attributed to a fast adsorption–desorption of phenol on the catalyst. This explanation was evidenced by simple exposing an aqueous phenol solution (100 ppm) to the catalyst for a period of 1 h applying the same conditions as used for degradation reactions. The variations of phenol concentration in such a system have been depicted in the inset of Fig. 2. It is clearly observed that phenol disappears quickly and then appears gradually until its initial concentration is apparently detected. In fact, by addition of the solution containing phenol to the catalyst, phenol is partially adsorbed on the support (alumina). In turn, owing to the low adsorption tendency of phenol on alumina [26], it returns to the solution as a reversible process and recreates the initial concentration of phenol. In presence of formic acid, due to the strong adsorption of carboxylic acid on alumina [27], the replacement of phenol molecules with formic acid's ones on the catalyst surface occurs and phenol releases back into the solution faster. Followed by the mentioned adsorption–desorption, by reducing the initial dose of formic acid the oxidation of phenol proceeds faster. The difference is obviously observed at 1 h, where remaining phenol, 62% for the reaction started with 500 mM formic acid drops to 36% for the reaction started with 40 mM formic acid. Finally, by arriving to the low concentration of phenol, the oxidation rate is retarded due to the kinetic aspects [28].

In order to compare the in situ generated H_2O_2 system with CFP, continuous and batch Fenton's reactions for phenol degradation were performed using the same reaction conditions as we used for the in situ ones. Firstly, the Fenton reactions were experienced using 300 ppm H_2O_2 continuously and batchwise. The results shown in Fig. 3A indicate disappearance of phenol in less than 3 h for the continuous run which corresponds to a mineralization of 31%. The oxidation was extended till 6 h resulting to maximum

48% mineralization. In the batch run (Fig. 3B), although a fast collapse of phenol is observed, mineralization did not go beyond 46% despite of lasting the reaction till 1 h. Increasing the H_2O_2 concentration to 600 ppm (1.2 times the stoichiometric amount required for complete mineralization of phenol) in continuous run (Fig. 3C) did not promote the yield of mineralization despite of faster oxidation of phenol. The batch reaction with 600 ppm (Fig. 3D) even arrived to worse result of mineralization that was 36% after 6 h. The reason of such a phenomenon has been already elucidated [29] by the fact that hydrogen peroxide acts as free-radical scavenger itself at high concentrations, thereby inhibits proceeding the oxidation process. Fig. 4 displays the corresponding final filtered solutions after the end of each reaction, i.e. in situ system (A), continuous (B) and batch (C) CFP using 300 ppm H_2O_2. In situ system degrades phenol through a slower but more controlled process which arrives to a nearly colorless solution. Continuous CFP, although is able to decompose the whole phenol at shorter time, eventually a pale brown solution remains which reflects the presence of toxic aromatic intermediates. The batch system also acts fast on phenol but lower mineralization and pale brown solution is obtained. It has been concluded that the observed color through a phenol degradation process depends on the level of oxidation achieved [30].

As it has been mentioned in the literature, one of the main drawbacks of Fenton's process is its weak capacity to degrade some of the intermediates which are produced during the phenol oxidation [31]. These compounds, which are known as recalcitrant, include mostly organic acids such as oxalic, maleic and acetic acids. As mineralization is mostly the result of oxidation of such organic acids to CO_2 and H_2O, it seems to be logical to state that the difference in mineralization between CFP and in situ system could be attributed to the ability of the later to degrade further the recalcitrant organic acids. However, this assumption needs further investigation to be properly approved.

Fig. 5 demonstrates phenol removal profile in the similar in situ system described above but without the presence of ferrous ion. 42% phenol degradation along with 6% mineralization is achieved, suggesting that hydrogen peroxide can oxidize phenol directly (ca. 10% in 2 h, results not shown) and especially that the catalyst can play the role of ferrous ion in converting H_2O_2 to hydroxyl radicals. In fact, in presence of ferrous ion, occurrence of the above phenomenon beside the formation of hydroxyl radical via Fenton's process can positively affect the general efficiency of the reaction.

Formic acid in this system behaves as a source of hydrogen to produce hydrogen peroxide, besides providing the necessary acidic pH. The compound can have another important advantageous side effect which has been proposed by Ferraz et al. [32]. It has been shown both computationally and empirically that organic acids and specifically formic acid can enhance the efficiency of Fenton's process in the degradation of organic compounds. In other words, formic acid can interact with H_2O_2 to lead to better formation of hydroxyl radical. Another promoter of the reaction can be oxygen which has been generally verified to be as supplemental bulk oxidant or rate accelerator [2]. However, exceptionally, in the case of formic acid, oxygen can play an inhibiting role by terminating the Fenton cycle [33].

The alumina supported-Pd catalyst used for this work shows excellent stability, since no Pd leached into the solution was detected by atomic absorption analysis after the end of each run. This advantage makes possible the recovery of the catalyst at the end of the reaction. The recovered and re-recovered catalysts by filtration and drying at 110 °C for 12 h were utilized for phenol degradation reaction and surprisingly displayed very interesting behaviour. These results have been shown in Fig. 6. Higher decomposition rate of formic acid is observed compared to the fresh catalyst, giving rise to an impact on phenol degradation.
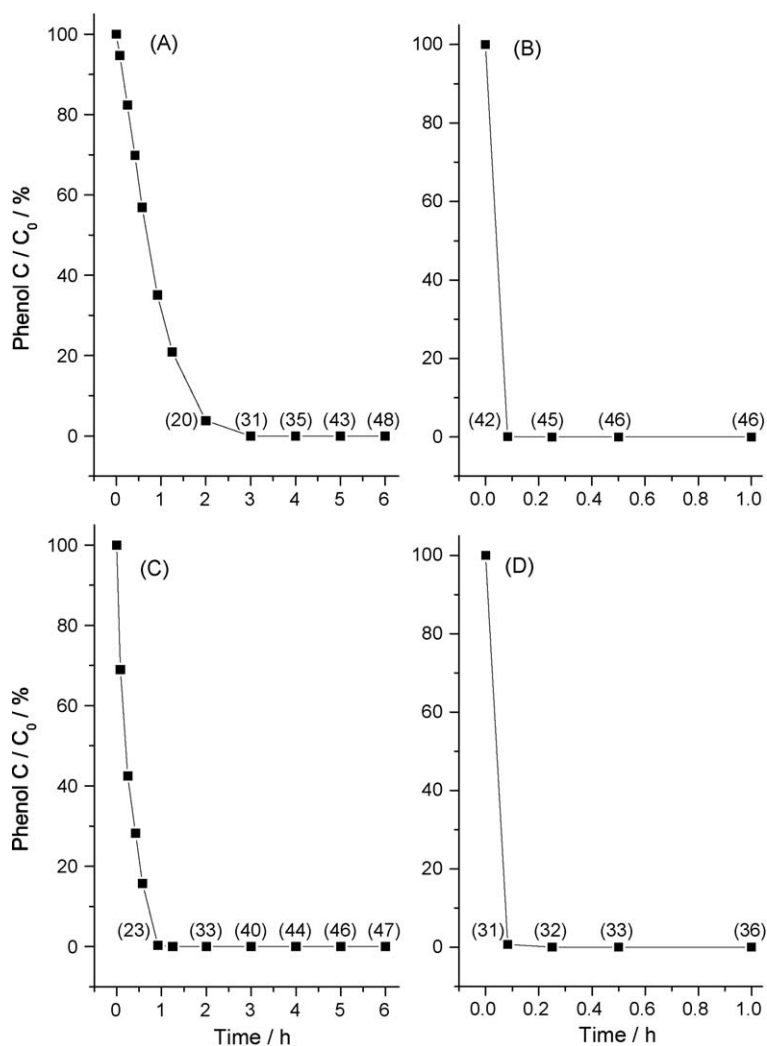
Fig. 3. (A) Phenol degradation profile by continuous CFP using 300 ppm H_2O_2; (B) phenol degradation profile by batch CFP using 300 ppm H_2O_2; (C) phenol degradation profile by continuous CFP using 600 ppm H_2O_2; (D) phenol degradation profile by batch CFP using 600 ppm H_2O_2; the numbers in parentheses are %TOC removed.
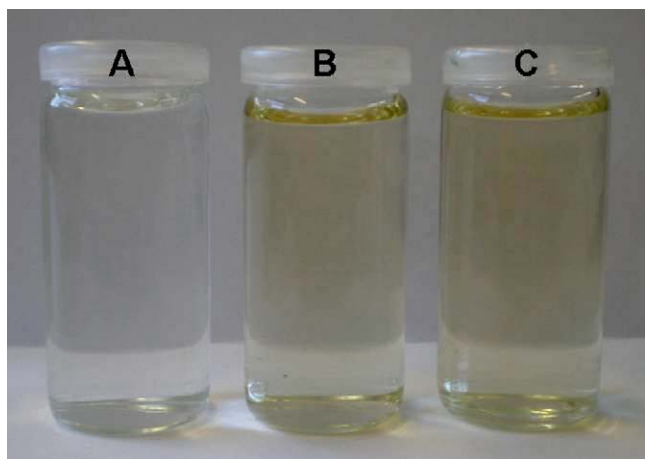

Fig. 4. Filtered solutions at the end of phenol degradation reactions obtained by (A) in situ system (100 mM initial concentration of F.A.); (B) continuous CFP (300 ppm H_2O_2); (C) batch CFP (300 ppm H_2O_2).
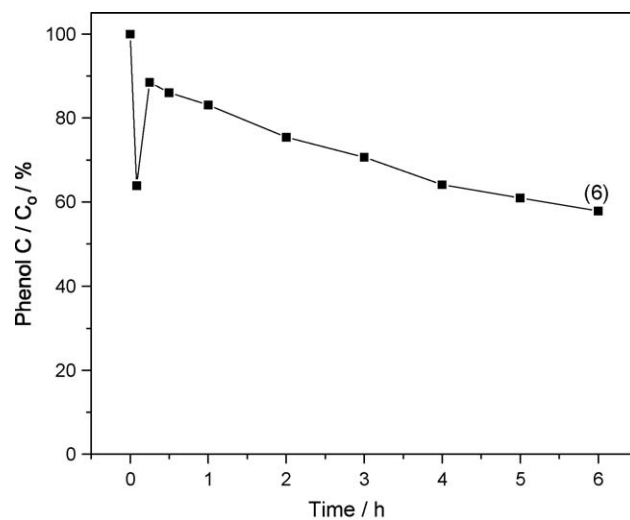
Fig. 5. Phenol degradation profile by in situ generated H_2O_2 in absence of ferrous ion (100 mM initial F.A. concentration); the number in parenthesis is %TOC removed.
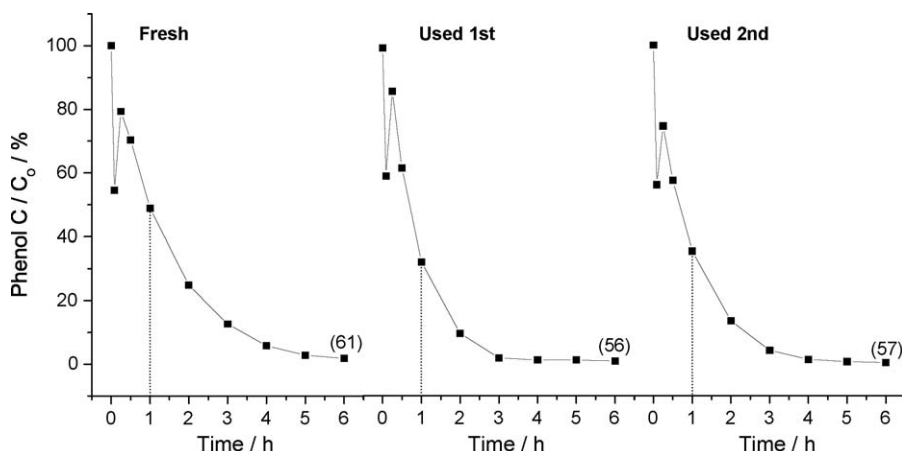
Fig. 6. Phenol degradation profile obtained by in situ generated H_2O_2 over fresh and used Pd5/Al catalyst (100 mM initial F.A. concentration). The numbers in parentheses are %TOC removed.

Nearly 70% conversion for phenol is attained within the first hour of the reaction. Nevertheless, mineralization achieved at the end of the reaction is a little lower in comparison with the fresh catalyst. The above phenomenon can be rationalized as the fresh Pd catalyst during the first run not only does not loose its activity but also improves it since the H_2 released from the decomposition of formic acid can re-reduce likely oxidized and even non-reduced Pd sites and avoid deactivation of the catalyst.

3.3. Evolution of intermediates

Different pathways have been proposed for oxidation of phenol in aqueous phase [34]. In general, phenol degradation pursues a sequential process passing through formation of several intermediates. In Fenton's process, initially phenol hydroxylation occurs which results in dihydroxylbenzenes such as hydroquinone, resorcinol and catechol [35]. Formation of resorcinol based on substitution rules in organic chemistry is implausible. These compounds undergo a further oxidation leading to quinone compounds which are: p-benzoquinone and o-benzoquinone. The later two quinones are in redox equilibrium with their corresponding hydroquinones [36]. In turn, phenolic ring is collapsed to produce low molecular weight carboxylic acids like maleic, oxalic and acetic acids which are mineralized to water and carbon dioxide. Fig. 7 displays concentration profile of catechol as representative of aromatic intermediate compounds. Catechol is more resistant to degradation than quinones [37] and therefore its variations during the reaction can be interesting. Moreover, in our system, we could not follow quantitatively the other aromatic intermediates by HPLC, because the retention times of hydroquinone and p-benzoquinone overlied on each other and their individual analysis was difficult. By starting the reaction, catechol is produced and its concentration within the reaction medium increases, which depends directly on the rate of phenol degradation. Gradually, catechol concentration undergoes decomposition and competes with its formation. Using 100 mM formic acid, the catechol concentration reaches to a maximum which then slips to near 1 ppm after 6 h. This peak corresponds to 50% degradation of phenol after 1 h reaction (see Fig. 2). With lower formic acid concentrations, higher amount of catechol is produced, up to nearly 30 ppm. Then, decomposition of catechol is predominant, leading to a decrease of its concentration down to 2–5 ppm after 6 h. Using 500 mM formic acid, catechol graph appears as a hillock form indicating that oxidation process is mild. The color changes during the degradation reaction can also reflect remediation of the intermediates which possess higher toxicity than phenol itself

[38]. In conventional Fenton, when the reaction is carried out batchwise, the color of the solution changes from colorless to dark brown as soon as the addition of hydrogen peroxide. The dark brown color gradually misses its intensity and after 1 h a pale brown color remains (Fig. 4C). The continuous Fenton's process indicates appearance of pale brown color by addition of hydrogen peroxide which is constant until the end of the reaction (Fig. 4B). The color can be arisen from different sources such as, the quinhydrone complex, the Fe^{3+}-catecholate complex, Fe^{3+}-oxalate complex and polymeric species resulted from aromatic condensations. At these conditions no peaks related to the above colored compounds are detected in the HPLC chromatogram. In our in situ H_2O_2 system, the solution is almost colorless at the end of the reaction after the catalyst filtration (Fig. 4A) which reflects higher capacity of the system to oxidize the aromatic intermediates. Therefore, it can be concluded that in situ generated H_2O_2 system is able to degrade phenol and its toxic intermediates with higher efficiency with respect to CFP.

3.4. Effect of temperature

Since both decomposition of formic acid and oxidation of phenol are promoted by elevating the temperature [39,29], we studied the effect of higher temperature on phenol degradation via
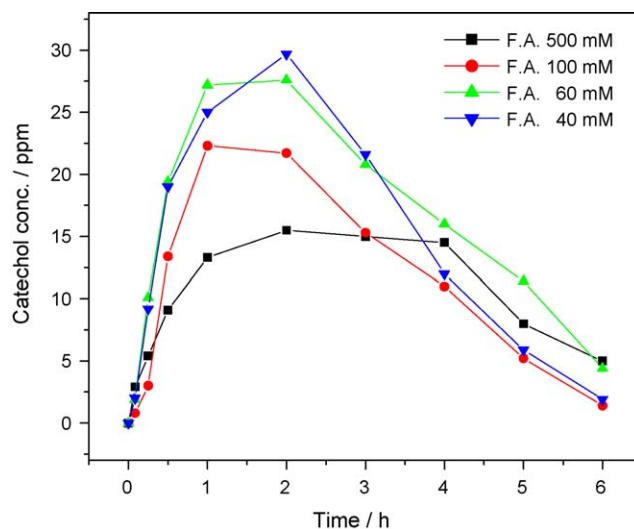

Fig. 7. Evolution of catechol during phenol degradation using different initial concentrations of formic acid.
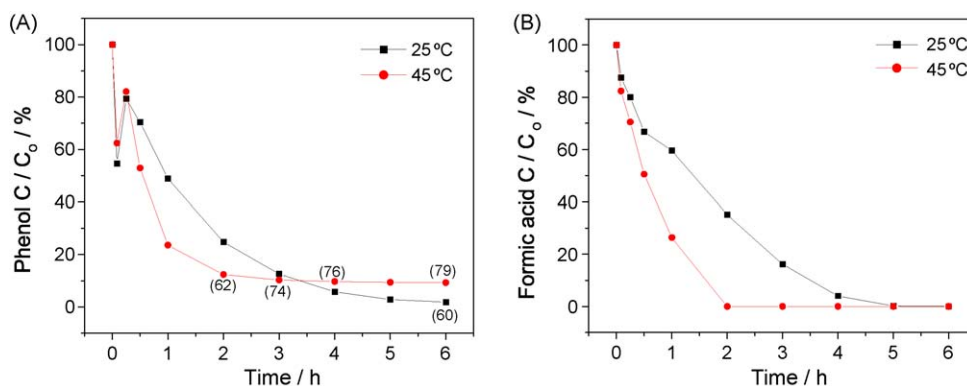
Fig. 8. (A) Phenol degradation profiles using in situ generated H_2O_2 over Pd5/Al at different temperatures (100 mM initial concentration of F.A.). (B) Formic acid decomposition profiles during the above reactions.

in situ generated H_2O_2 reaction. Fig. 8 illustrates a comparison between phenol and formic acid decomposition carried out at 25 and 45 °C. Increasing the temperature to 45 °C gives rise to decomposition of formic acid with higher rate than that at 25 °C. Further decomposition of formic acid generates more H_2O_2 which subsequently decomposes with promoted rate. As it is observed, after 1 h, the oxidation of phenol reaches to nearly 75%, but, by termination of formic acid after 2 h, oxidation of phenol is suppressed and around 9 ppm of phenol remains at the end of the reaction. After 2 h 62% as TOC removed is obtained, while at ambient condition and with the same initial dose of formic acid, 6 h are needed to achieve this degree of mineralization. At 45°, after the termination of formic acid, mineralization proceeds up to 79% after 6 h. The same phenomenon was observed for the systems started with 40 and 60 mM (Section 3.2) formic acid at ambient conditions. The interesting point is that phenol is not affected by the catalyst after termination of formic acid, indicating possible degradation of aromatic intermediates and carboxylic acids. By comparison of the high temperature system with that at ambient, it can be simply viewed that at 45 °C almost similar efficiency is achieved but three times faster than 25 °C considering mineralization as measure.

3.5. Effect of Pd content

As it has been mentioned in our recent report [21], decreasing of Pd content over alumina can enhance the
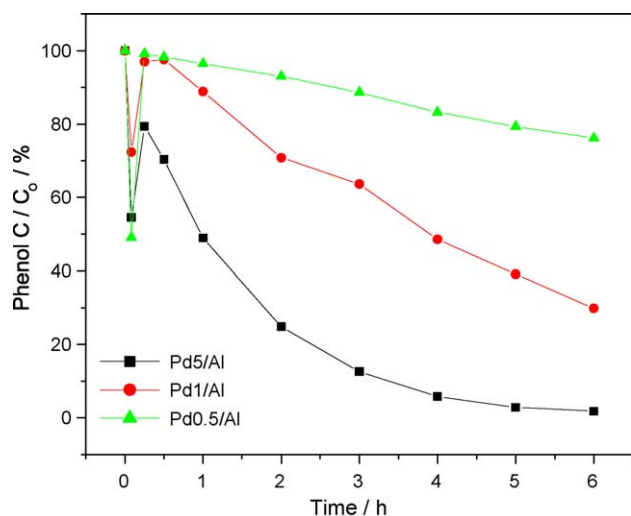
productivity for direct formation of hydrogen peroxide, in particular for bulk purposes. Since for in situ application a catalyst with ability to produce hydrogen peroxide at short time is anticipated to be more desired, we fulfilled our reactions using Pd5/Al catalyst. In order to evidence the above view, we tested the lower Pd content catalysts for phenol degradation via in situ generated hydrogen peroxide. The results displayed in Fig. 9 indicate that by decreasing Pd content, phenol degradation rate reduces. For example, the Pd0.5/Al catalyst, which had represented highest productivity within 1 h, could not compete with Pd5/Al and a maximum of 24% for phenol degradation after 6 h is yielded. These observations support the idea previously suggested (Section 3.1) that real production rate of hydrogen peroxide for the Pd5/Al catalyst should be displayed by extrapolating the production rate passing from zero point and 5 min (as shown in Fig. 1). On the way to support the above assumption, the productivity of hydrogen peroxide production obtained as in situ (300 ppm) is more than one order of magnitude higher than that of direct generation (24 ppm) after 6 h, considering as well that 100 mM formic acid was used for the in situ system with respect to 500 mM for direct generation.

4. Conclusions

We applied hydrogen peroxide generation via oxygen and formic acid system to produce hydrogen peroxide in situ for degradation of phenol by Fenton's reaction. The system indicated significant ability to mineralize phenol and its intermediates. A maximum of 60% mineralization was achieved in comparison with the 48% obtained by the simulated continuous and 46% by batch CFP. These results can highlight the advantage of in situ approaches for the oxidation process with respect to even continuous feeding of the oxidant. The productivity of hydrogen peroxide during in situ generation is remarkably enhanced compared to the direct process for bulk production. The catalyst possesses excellent stability as no Pd leached was detected at the end of each run. In addition, repeatability of the catalyst is significant as it shows almost the same activity by performing the reaction twice with the recovered catalyst.

Fig. 9. Phenol degradation profiles by in situ generated H_2O_2 using different Pd loaded catalysts.

References

[1] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, Catal. Today 53 (1999) 51–59.
[2] J.J. Pignatello, E. Oliveros, A. MacKay, Crit. Rev. Environ. Sci. Technol. 36 (2006) 1–84 (and references therein).
[3] S. Esplugas, J. Giménez, S. Contreras, E. Pascual, M. Rodríguez, Water Res. 36 (2002) 1034–1042.
[4] C.W. Jones, Applications of Hydrogen Peroxide and Derivatives, RSC, 1999, pp. 207–230.
[5] T. Tatsumi, K. Yuasa, H. Tominaga, J. Chem. Soc., Chem. Commun. (1992) 1446–1447.
[6] M.G. Clerici, P. Ingallina, Catal. Today 41 (1998) 351–364.
[7] R. Meiers, U. Dingerdissen, W.F. Hölderich, J. Catal. 176 (1998) 376–386.
[8] R. Meiers, W.F. Hölderich, Catal. Lett. 59 (1999) 161–163.
[9] E.D. Park, Y.-S. Hwang, J.S. Lee, Catal. Commun. 2 (2001) 187–190.
[10] J.R. Monnier, Appl. Catal. A: Gen. 221 (2001) 73–91.
[11] S. Niwa, M. Eswaramoorthy, J. Nair, A. Raj, N. Itoh, H. Shoji, T. Namba, F. Mizukami, Science 295 (2002) 105–107.
[12] J.E. Remias, T.A. Pavlosky, A. Sen, J. Mol. Catal. A: Gen. 203 (2003) 179–192.
[13] G.D. Vulpescu, M. Ruitenbeek, L.L. van Lieshout, L.A. Correia, D. Meyer, P.P.A.C. Pex, Catal. Commun. 5 (2004) 347–351.
[14] G. Li, J. Edwards, A.F. Carley, G. Hutchings, Catal. Commun. 8 (2007) 247–250.
[15] J.J. Bravo-Suárez, K.K. Bando, T. Akita, T. Fujitani, T.J. Fuhrer, S.T. Oyama, Chem. Commun. (2008) 3272–3274.
[16] J.J. Bravo-Suárez, K.K. Bando, T. Fujitani, S.T. Oyama, J. Catal. 257 (2008) 32–42.
[17] J.M. Campos-Martin, G. Blanco-Brieva, J.L.G. Fierro, Angew. Chem. Int. Ed. 45 (2006) 6962–6984.
[18] J.H. Lunsford, J. Catal. 216 (2003) 455–460.
[19] V.R. Choudhary, C. Samanta, P. Jana, Chem. Commun. (2005) 5399–5401.
[20] V.R. Choudhary, P. Jana, Catal. Commun. 8 (2007) 1578–1582.
[21] M.S. Yalfani, S. Contreras, F. Medina, J. Sueiras, Chem. Commun. (2008) 3885–3887.
[22] Y.-G. Zhang, L.-L. Ma, J.-L. Li, Y. Yu, Environ. Sci. Technol. 41 (2007) 6264–6269.
[23] I. Sirés, F. Centellas, J.A. Garrido, R.M. Rodríguez, C. Arias, P.L. Cabot, E. Brillas, Appl. Catal. B: Environ. 72 (2007) 373–381 (and references therein).
[24] G. Bergeret, P. Gallezot, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 2, Wiley-VCH, 1997, p. 439.
[25] Y.-F. Han, N. Phonthammachai, K. Ramesh, Z. Zhong, T. White, Environ. Sci. Technol. 42 (2008) 908–912.
[26] C.M. Cirtiu, H.O. Hassani, N.-A. Bouchard, P.A. Rowntree, H. Ménard, Langmuir 22 (2006) 6414–6421.
[27] J.T. Hall, K.P. Hansma, Surf. Sci. 76 (1978) 61–76.
[28] N. Kang, D.S. Lee, J. Yoon, Chemosphere 47 (2002) 915–924.
[29] R. Alnaizy, A. Akgerman, Adv. Environ. Res. 4 (2000) 233–244.
[30] F. Mijangos, F. Varona, N. Villota, Environ. Sci. Technol. 40 (2006) 5538–5543.
[31] R.J. Bigda, Chem. Eng. Prog. (1995) 62–66.
[32] W. Ferraz, L.C.A. Oliveira, R. Dallago, L. da Conceição, Catal. Commun. 8 (2007) 131–134.
[33] C.K. Duesterberg, W.J. Cooper, T.D. Waite, Environ. Sci. Technol. 39 (2005) 5052–5058.
[34] A. Santos, P. Yustos, A. Quintanilla, S. Rodríguez, F. García-Ochoa, Appl. Catal. B: Environ. 39 (2002) 97–113.
[35] J.A. Zazo, J.A. Casas, A.F. Mohedano, M.A. Gilarranz, J.J. Rodríguez, Environ. Sci. Technol. 39 (2005) 9295–9302.
[36] H. Alt, H. Binder, A. Köhling, G. Sandstede, Angew. Chem. Int. Ed. 10 (1971) 514–515.
[37] D.H. Bremner, A.E. Burgess, D. Houllemare, K.-C. Namkung, Appl. Catal. B: Environ. 63 (2006) 15–19.
[38] A. Santos, P. Yustos, A. Quintanilla, F. García-Ochoa, J.A. Casas, J.J. Rodríguez, Environ. Sci. Technol. 38 (2004) 133–138.
[39] E.M. Cordi, J.L. Falconer, J. Catal. 162 (1996) 104–117.